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Rapid thermal processing of CuAlSe₂

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Abstract

CuAl thin film metallic precursors were selenised using a tube furnace or a rapid thermal processor (RTP). A comparison is made between the two processes for slightly Cu rich films and best crystallographic and elemental properties are obtained for films selenised by RTP: it was found that ternary compound could only be formed using the RTP. In both cases a large amount of Cu_xSe_y grains are found to develop at the surface of the films. Only samples processed in the RTP showed cathodoluminescence excitation at 2.68 eV characteristics of the electronic bandgap. Al rich samples were used to study the effect of etching the Cu_xSe_y phases from the surface in order to reveal the underlying CuAlSe₂ material.

1. Introduction

Thin film solar cells based on I-III-VI₂ semiconductors, such as Cu(In,Ga)(S,Se)₂ (CIGS) have reached record efficiency of 20% [1]. The technology is currently limited by a p-type absorbing material with a relatively low bandgap (~1.15 eV) [2] compared to the theoretical optimum of 1.5 eV [3] and by the use of a cadmium based n-type buffer layer [2]. Alternative buffer layers can be successfully used such as In₂S₃ [4], In_xSe_y [5], ZnS [6], ZnSe [7], ZnO [8] and ZnMgO [9].

CuAlSe₂ (CAS) is another I-III-VI₂ semiconductor which has suitable properties for use as a window layer. CuAlSe₂ has an energy bandgap of 2.67 eV [10], and crystallizes with the chalcopyrite structure making the semiconductor a good lattice match for the underlying CIGS absorber. Finally, CAS film can be intrinsically doped either p or n type by control of the Cu/Al ratio in the film [11, 12] yielding the possibility to create either a wide bandgap absorber or window layer.

However this material is difficult to grow due to the presence active Al. In this work

we investigate a route to produce CAS films using a 2-stage process similar to that use in the production of CIGS films [13] and we present initial results.

2. Experimental

CAS films were produced by a 2-stage process by means of selenisation of magnetron sputtered Cu-Al metallic precursors. The Cu and Al layers were sequentially sputter deposited using high purity (5N) targets onto unheated soda-lime glass or Mo-coated soda lime glass substrates, placed on a rotating substrate table. This was followed by selenisation either in a tube furnace (slow process) or using a rapid thermal processor (fast process). The slow process involved selenisation in a mixed H₂/N₂ (10 mbar) and elemental selenium atmosphere at temperatures of up to 550°C (ramp 15°C min⁻¹) for up to 120 min. The fast process involved heating the precursor up to 550°C in 60-90 seconds and holding this temperature for 1-5 min under high Ar pressure (500-800 mbar) and elemental selenium. When necessary the films were etched for 90 sec using a 10% concentrated KCN solution.

The structural quality of the absorber layers was examined using X-ray diffraction (XRD) carried out with a Siemens D-5000 diffractometer using a CuK α radiation source ($\lambda = 1.5406 \text{ \AA}$). In order to obtain information about the surface morphology and the composition of the layers, secondary electron images were taken and wavelength dispersive X-ray (WDX) analysis was performed using a Cameca SX100 electron microprobe modified for cathodoluminescence (CL).

3. Results & Discussion

The CuAl precursors were grown either slightly Cu-rich (Cu/Al = 1.04) on Mo coated glass as potential p-type absorber (type A) or Al rich (Cu/Al = 0.75) on glass as potential n-type window layers (type B).

The layers were terminated with a 5 nm thick Cu layer to reduce the oxidation of the precursors. The thickness of the precursors was around 600 nm. The XRD pattern of a type A film is shown in figure 1 (a). The phases presents are Al, Cu and CuAl_2 , indicating partial mixing of the two elements. No oxides were detected in the bulk of the film.

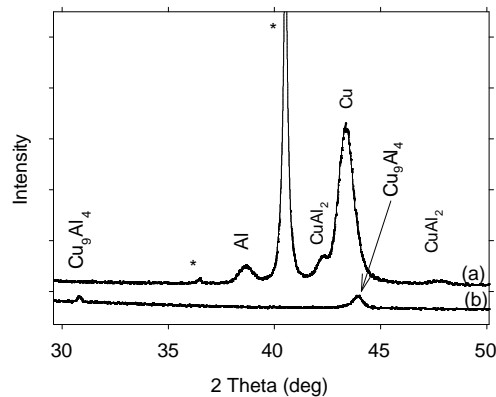


Figure 1. XRD patterns of type A (a) and type B (b) CuAl precursor. Peaks marked (*) arise from the substrate.

The XRD patterns of selenised type A films are shown in figure 2 for both the slow and fast process. Using the slow process it is possible to form some CAS material however the film is dominated by Cu_xSe_y phases and unreacted CuAl. When using the faster heating process the CAS

phase dominates the film crystallography and all the precursor is found to react with the chalcogen. The CAS film is shown to crystallize with the chalcopyrite structure which is indicated by the presence of the smaller (103) reflection.

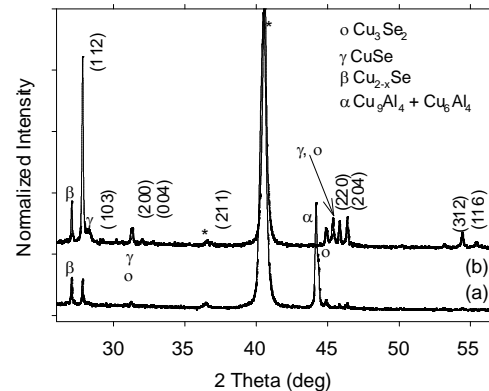


Figure 2. XRD patterns of a selenised CuAl film (type A) using a slow process (a) and a fast process (b). Peaks marked (*) arise from the substrate.

Figure 3 shows the surface morphology of the selenised type A films and WDX line scans (marked as a white line in secondary electron images). The flat and smooth surface of the precursor film (not shown here) gives way to a film which displays large numbers of surface features and not the granular structure usually found in thin film solar cell absorbers.

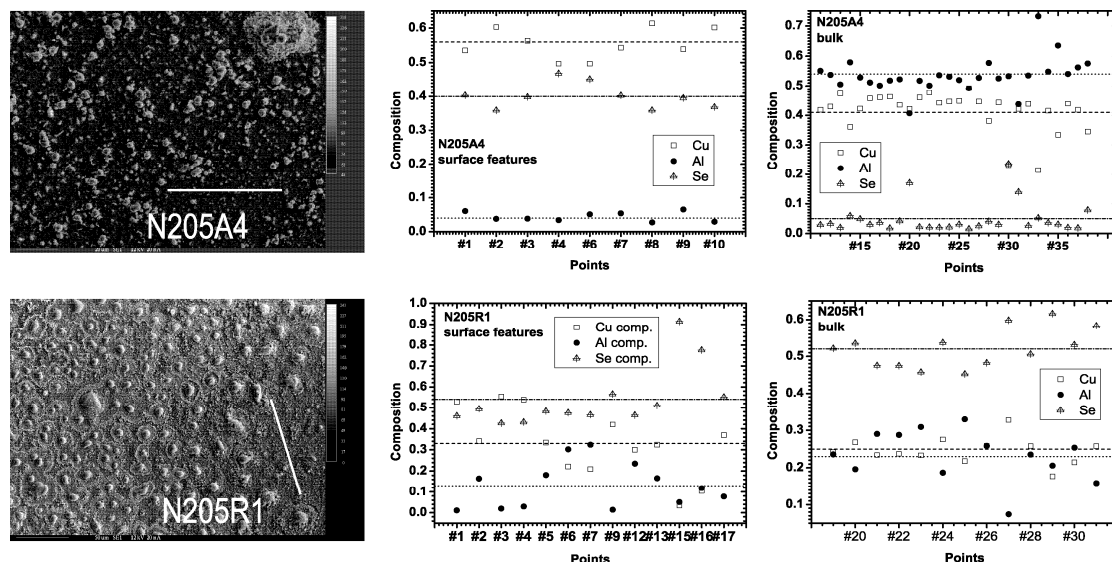


Figure 3. SEM micrographs (left), and WDX line scans (marked in the SEM images) of surface features (middle) and bulk film composition (right) of selenised CuAl films for a slow process (top) and fast process (bottom). The lines in the plots of the elemental composition display the average content of all points for each element (Cu: dashed, Al: dotted and Se: dashed-dotted) and act as a guide for the eyes.

The middle column of figure 3 shows the composition of surface features while the right column gives the composition of the bulk of the film. For the slow process the surface features are consistent with either CuSe or Cu₃Se₂ in accordance with the XRD measurements; while for the fast process varied composition is detected: some CuSe elements, some nearly pure Se grains and some mixed ternary CuAlSe₂ grains.

The bulk composition of the films is shown in the right column of figure 3. The scans corresponding to the slow process clearly indicate that the Se incorporation is close to zero with an average film composition of Cu_{0.41}Al_{0.54}Se_{0.05} (with an uncertainty of 0.01). On the other hand the line scan corresponding to the CuAl film selenised using the fast process shows an average composition of Cu_{0.25}Al_{0.23}Se_{0.52}, indicating a good homogeneity of the ternary CAS compound. However care should be taken because other line scans showed less uniform compositions.

All films showed a high level of oxygen content and levels up to four times higher in the films selenised using the slow process. However no oxide phase either Cu or Al based were detected on the XRD patterns.

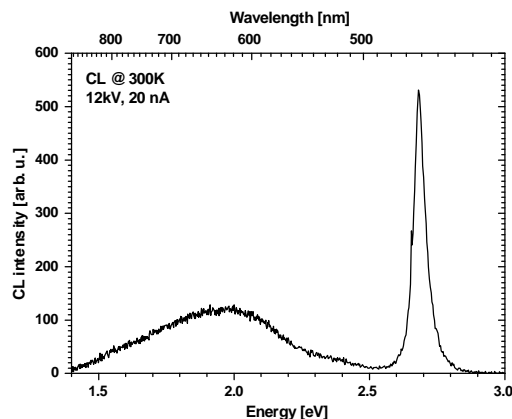


Figure 4. Room temperature CL spectrum of type (A) CuAl precursor film selenised using the fast process.

In addition to the compositional data, CL was measured for the CAS layers produced by the fast process. The room temperature spectrum is displayed in figure 4. A peak at 2.68 eV with a full width at half maximum of 57 meV dominates the spectrum. This peak corresponds to band edge luminescence of the CuAlSe₂ layer. No CL spectrum could be obtained for the layer formed in the slow process since it consists mainly of copper and aluminium.

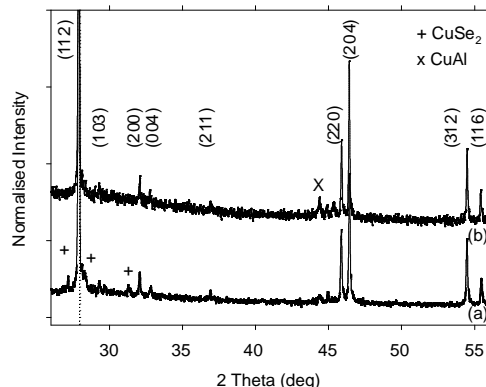


Figure 5. XRD patterns normalized against the (112) reflection of CAS before (a) and after etching (b).

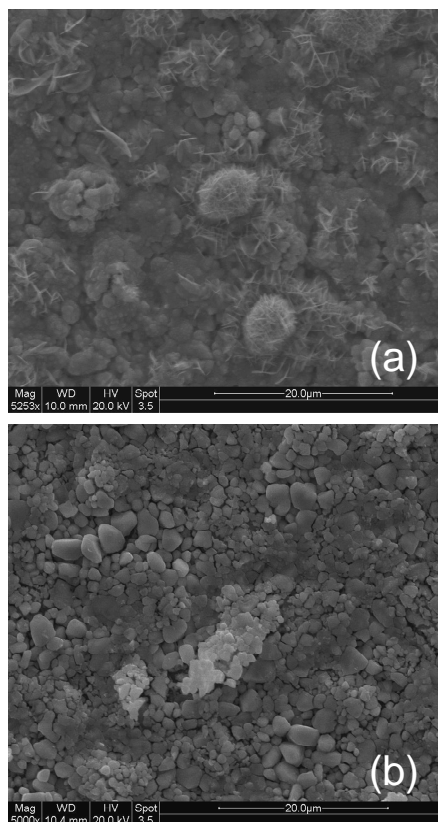


Figure 6. Secondary electron micrographs of CAS films before (a) and after etching (b).

The XRD pattern for a type B precursor is shown in figure 1 (b). Although the films were grown Al rich (Cu/Al = 0.75) the only detected phase was Cu₉Al₄. Type B precursor films were exclusively selenised using the fast process and in order to remove the Cu_xSe_y phases, a cyanide etch was performed. After this treatment the dark grey films evolved into yellow films which are characteristic of a wide bandgap material. Figure 5 shows the XRD patterns

for a CAS film on glass pre and post-etching. After etching most peaks corresponding to the Cu_xSe_y phases disappeared indicating the effectiveness of the cyanide etch.

The effect of etching is also observed on the surface morphology of the films. Figure 6 displays the corresponding secondary electron micrographs for an unetched and etched layer. The non uniform surface with large agglomerate of Cu_xSe_y grains gives way to a smoother film after etching. Compact, micron sized grains are revealed. However the films turned out to be pinholed and extremely thin preventing effective optical or electrical characterization.

4. Conclusion

CuAlSe_2 films were produced by a 2-stage process using a rapid thermal annealing of magnetron sputtered CuAl metallic precursor. Films crystallize in the chalcopyrite structure but surface coverage is dominated by Cu_xSe_y grains. As with $\text{CuIn}(\text{Se},\text{S})_2$ those grains can easily be removed when performing a cyanide etch. Further experiments are in progress in order to increase the surface coverage of the CAS layer by using thicker films and also by altering the etching recipe.

Acknowledgments

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